COMMONWEALTH OF MASSACHUSETTS
DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF WASTE SITE CLEANUP

ISSUES PAPER

IMPLEMENTATION OF

VPH/EPH APPROACH

PUBLIC COMMENT DRAFT

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TABLE OF CONTENTS

IMPLEMENTATION OF VPH/EPH APPROACH

BACKGROUND AND OBJECTIVES

In a document dated August 1994, the Massachusetts Department of Environmental Protection (MADEP) proposed a new toxicological approach to characterize petroleum contaminated media. Under this approach, the toxicity of petroleum contaminated media is defined by (a) the individual concentrations of targeted petroleum constituents, such as BTEX and PAH compounds, and (b) the collective concentrations of (remaining) aliphatic and aromatic hydrocarbons, within defined carbon ranges.

To provide data to support and complement this new toxicological approach, MADEP issued two draft analytical methods in August 1995. Two methods were needed to cover the range of hydrocarbons of concern, both "Volatile Petroleum Hydrocarbons" (VPH), and "Extractable Petroleum Hydrocarbons" (EPH). Comments on these draft methods are currently under review within the agency.

The use and implementation of the new toxicological approach and analytical methodologies raise a number of application and operational issues and concerns, ranging from the philosophical to the technically mundane. The purpose of this paper is to identify the major items of concern, discuss issues and resolution options, and, where appropriate, recommend a course of action.

The major items of concerns can be bifurcated into two distinct categories:

- Issues concerning the derivation of Method 1 VPH/EPH Standards; and
- Issues concerning the use and application of the new approach and methods.

INFORMATION SOURCES

Several resources and citations referenced in this document warrant explanation:

(1) TOTAL PETROLEUM HYDROCARBON CRITERIA WORKING GROUP

The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) is a national consortium of state regulatory agencies, academia, DOD, DOE, USEPA, ASTDR, petroleum, power and transportation industries, and consulting firms. Massachusetts is among the states participating in this organization.

The goal of this group is to evaluate and propose methods to characterize risks posed by petroleum contaminated media. Recently, TPHCWG has released a series of draft documents and proposals concerning the toxicology and fate of petroleum products. Final reports are expected within 4 months.

Two aspects of the TPHCWG efforts have relevance to this Issue Paper:

- After evaluating all existing and proposed methodologies, and after conducting an extensive literature search, TPHCWG has determined that a surrogate/indicator approach, similar to the August 1994 MADEP proposal, is the most appropriate means to characterize human health risks posed by petroleum hydrocarbons released to the environment. A risk assessment approach proposed by TPHCWG is identical or similar to the MADEP method in most respects. Such a proposal provides independent and national affirmation of the approach that has been developed and pursued by MADEP.

- TPHCWG has also conducted extensive research into the composition and fate of petroleum products and hydrocarbons, and has assembled, derived, and tabulated physical/chemical properties for over 260 petroleum constituents. Moreover, TPHCWG has recently proposed a method to develop range-specific properties and parameters which can be used to model the fate and transport of aliphatic and aromatic fractions of interest. This data and approach have been used by MADEP in developing the proposals contained in this Issues Paper.

MADEP is continuing to evaluate work products produced by TPHCWG, and may refine some elements of the toxicological approach and/or modify surrogate Reference Doses based upon their findings and recommendations.

(2) UNPUBLISHED SOURCES

Information sources cited in this document to support discussion elements and/or recommendations include 4 unpublished and/or draft documents that are not widely available:

- <u>TPHCWG Draft Report</u> - In a draft report dated June 1995, revised 4/12/96, TPHCWG has provided a tabulation of physical/chemical properties for over 260 petroleum constituents, and proposed a series of algorithms relating physical/chemical properties to the molecular weight of aliphatic and aromatic compounds and fractions.

- <u>Natick UST Project</u> - During 1994, 320 underground storage tanks (USTs) containing #2 fuel oil were removed from residential properties in Natick, Massachusetts, as part of a systematic effort to eliminate threats to the town's water supply. All removals were overseen and monitored by a single consulting company (Whitman and Howard), using protocols and procedures approved by MADEP. This project provided a unique opportunity to assemble a large universe of assessment data and observations, which was obtained and documented in an approved, consistent, and comparative manner, including:

  o 242 soil samples for odor/staining observations;
  o 239 soil samples for VOC headspace analysis;
  o 224 soil samples for TPH analysis;
  o 84 soil samples for BTEX analysis; and
  o 29 soil samples for PAH analysis.

- UMass Petroleum Report - Under contract to MADEP, the University of Massachusetts at Amherst (UMass/Amherst) prepared a draft document on petroleum products and toxicities, circa 1986. A limited number of citations have been referenced from this draft.

- VPH and EPH Sample Data - Since the release of the draft VPH and EPH analytical methods in August, 1995, a limited number of actual field samples have been analyzed by commercial laboratories. This data provides valuable information relating traditional "TPH" concentration values to VPH and EPH levels, and provides insight into some of the issues discussed in this paper.

RCNI CONCEPT AND TERMINOLOGY

Throughout this document, aliphatic and aromatic fractions are differentiated on the basis of their molecular weight or "carbon" ranges, e.g., C_5-C_8 Aliphatic Hydrocarbons. In using this terminology, certain liberties have been taken, relative to the **precise** composition of the hydrocarbon fraction of concern.

Specifically, most analytical methods (including the proposed MADEP methods) employ chromatographic techniques that segregate hydrocarbons on the basis of boiling points, not carbon numbers. Thus, the "C_5-C_8 Aliphatic Hydrocarbons" quantitated by the proposed MADEP VPH method actually include some C_4 and C_9 aliphatics, and exclude some C_5 and C_8 aliphatics (e.g., branched chain alkanes typically elute before the normal alkane, aromatics after the normal alkane). As a further element of uncertainty, substituted aromatic compounds may be identified as either aliphatic or aromatic in nature, depending upon the specific analytical method employed.

While the implicit uncertainties inherent in grouping petroleum hydrocarbons in this manner should be understood and acknowledged, they are not deemed to be a significant methodological concern or limitation, given all the other uncertainties intrinsic to site and risk characterization processes. Nevertheless, for the purposes of calculating and designating fractional properties, a common "benchmark" sorting of compounds would be desirable.

Towards this end, TPHCWG has suggested an approach to address and model the fate of petroleum hydrocarbons and fractions, on the basis of "Relative Carbon Number Index" or RCNI[1]. The RCNI is defined as the carbon number of a compound normalized to the boiling point of normal alkanes. This relationship was empirically derived by plotting hydrocarbons by boiling point and carbon number. As an illustration, n-hexane contains 6 carbons and has a boiling point of 69 $^\circ$C; its RCNI is 6.0. Benzene, also containing 6 carbons, has a boiling point of 80 $^\circ$C; its RCNI is 6.5.

The RCNI of a compound can be roughly approximated by the following equation:

$$RCNI = 4.12 + [0.02][BP] + [6.5\ EE\ -5][BP]^2 \qquad \textbf{[1]}$$

where:

RCNI = Relative Carbon Number Index
BP = Boiling Point ($^\circ$C)

By using the RCNI methodology, individual compounds and collective hydrocarbon ranges can be readily categorized by boiling point. More importantly, TPHCWG has determined that a number of key physical and chemical properties of hydrocarbon compounds appear to be predictably related to the RCNI. On this basis, algorithms have been developed relating vapor pressures, solubilities, partition coefficients, and Henry's Law constants to the Relative Carbon Number Index of aliphatic and aromatic compounds. Using this technique, fate and transport properties can be estimated for any given aliphatic or aromatic hydrocarbon, or any given range of aliphatic and aromatic hydrocarbons.

DERIVATION OF METHOD 1 STANDARDS

The Massachusetts Contingency Plan (MCP) allows for the use of three methods to characterize risks posed at and by a site, and determine "how clean is clean enough". The easiest, and by far most commonly used option, is "Method 1". Under Method 1, MADEP has developed semi-generic cleanup standards for 105 common environmental contaminants, including "TPH". A Method 2 approach allows for the incorporation of site-specific contaminant fate and transport considerations; a Method 3 approach allows for completely site-specific risk characterizations. This tiered approach and process is similar to the (subsequently issued) ASTM "RBCA" concept.

Method 1 standards are risk-based, and consider a number of exposure pathways, including direct human contact, leaching to groundwater, vapor discharge to buildings, and ecological impacts. Moreover, certain "ceiling levels" are imposed to address concerns, like staining and odors, that are not otherwise addressed via conventional risk assessment techniques.

The human health component of individual Method 1 standards are set at an excess lifetime cancer risk (ELCR) limit of one-in-one-million, and/or Hazard Index (HI) of 0.2. Three groundwater categories/standards have been established: (1) GW-1, applicable at sites located on aquifers used for drinking water purposes; (2) GW-2, applicable at sites proximate to occupied buildings, where off-gassing of volatile contaminants is a possibility, and (3) GW-3, the default groundwater category applicable at all sites.

Three soil categories have also been established, based upon potential accessibility and frequency-of-exposure. These categories range from S-1, the most protective category (e.g., residential exposures), to S-3, which are isolated or deep soils. Given the three groundwater and three soil categories, a matrix of 9 Method 1 soil standards have been developed (e.g., S-1/GW-1, S-1/GW-2, etc.). Complete details on developmental parameters and assumptions for all Method 1 Standards are provided in MADEP publication "Background Documentation for the Development of the MCP Numerical Standards", dated April, 1994.

The current Method 1 "TPH" standard assumes a 50% hexane and 50% pyrene mixture, and is therefore overly conservative in most situations. Conversely, the current standard is limited to C_{10} and heavier hydrocarbons; lighter (gasoline range) hydrocarbons are not addressed. To better define and address risks at petroleum contaminated sites, MADEP is considering the development and issuance of revised Method 1 "TPH" standards. At issue are a number of developmental and regulatory concerns, discussed in more detail below.

(1) LEACHING CONSIDERATIONS

ISSUE: How should leaching concerns be incorporated into the new VPH/EPH approach and cleanup numbers?

DISCUSSION: The toxicological approach proposed previously by MADEP has only addressed those risks posed to human receptors via direct contact. To address all risks posed by hydrocarbon contaminants in soil, and derive Method 1 soil cleanup standards, an evaluation of leaching concerns must be undertaken.

TPHCWG has proposed that the average properties of aliphatic and aromatic hydrocarbons within defined carbon ranges be used as a surrogate representation of the fate and transport characteristics of that fraction. This differs somewhat from the toxicological surrogate approach used by MADEP, where an actual compound was selected as a "worst case" representation of a hydrocarbon fraction.

Also at issue is the number of hydrocarbon fractions which should be designated for the purposes of characterizing fate and transport concerns. A draft TPHCWG report has concluded that, excluding benzene and toluene, 11 distinct breakdowns become apparent when comparing and plotting properties vs structure/molecular weight[1]. Within each breakdown, physical/chemical properties were found to be consistent within approximately one order of magnitude. Similar to toxicological evaluations, this division is centered on the classification of the compound as aliphatic or aromatic, and molecular weight.

RECOMMENDATION: The use of an "average" surrogate approach is recommended. The selection of a single "worst case" fate and transport surrogate compound is deemed overly conservative, as significantly more data is available defining the physical properties of compounds than is available defining their toxicological properties. Moreover, such physical properties are perhaps more predictably related to hydrocarbon class and molecular weight.

Although 11 fate and transport fractions have been recommended by TPHCWG, for the sake of simplicity, it is recommended that MADEP consolidate these 11 fractions into the 6 fractions already designated by toxicological characteristic, i.e., C_5 - C_8 Aliphatics, C_9 - C_{12} Aliphatics, C_9 - C_{10} Aromatics, C_9 - C_{18} Aliphatics, C_{19} - C_{35} Aliphatics, and C_{10} - C_{22} Aromatics. Consolidation in this manner, however, will group compounds possessing fate and transport properties that vary over several orders of magnitude. To insure conservative values, it is recommended that the surrogate fractional properties be "weighted" toward the more mobile (lighter) ends.

This consolidation is proposed **only for the development of (generic) Method 1 standards**. Parties electing to conduct a more site-specific and less conservative Method 3 evaluation will have the option to incorporate and utilize all fractions recommended by TPHCWG.

Mobility Constants

TPHCWG has determined the following correlations between the Relative Carbon Number Index (RCNI) and mobility:

$$\log_{10} H = [0.02][RCNI] + 1.6 \quad \text{(aliphatics, } R^2 = 0.03) \quad \textbf{[2]}$$

$$\log_{10} H = [-0.23][RCNI] + 1.7 \quad \text{(aromatics, } R^2 = 0.84) \quad \textbf{[3]}$$

$$\log_{10} K_{oc} = [0.45][RCNI] + 0.43 \quad \text{(aliphatics, } R^2 = 0.94) \quad \textbf{[4]}$$

$$\log_{10} K_{oc} = [0.10][RCNI] + 2.3 \quad \text{(aromatics, } R^2 = 0.81) \quad \textbf{[5]}$$

where:

H = Henry's Law Constant, dimensionless
K_{oc} = organic carbon partition coefficient, mL/g
RCNI = Relative Carbon Number Index

Although there is not a good statistical correlation between the RCNI and Henry's Law constant for aliphatic compounds, it should be noted that such compounds have little affinity for the aqueous phase, and the (dimensionless) Henry's Law value is generally between 50 and 70.

Using the data and algorithms provided by TPHCWG, the recommended fate and transport surrogate values for the 6 hydrocarbon fractions of concern are presented in Table 1. Note that no values are recommended for C_{19}-C_{35} Aliphatics, as these compounds are essentially immobile in the environment.

Table 1 - Proposed Fate and Transport Surrogate Values

HYDROCARBON RANGE	AVERAGE/ DESIGNATED FRACTIONAL RCNI[a] VALUE	PROPOSED VALUES	
		H*	Koc**
C_5-C_8 Aliphatics	6.5	**54**	**2265**
C_9-C_{12} Aliphatics	10.5	**65**	**1.5 EE 5**
C_9-C_{10} Aromatics	9.5	**0.33**	**1778**
C_9-C_{18} Aliphatics	12.0[b]	**69**	**6.8 EE 5**
C_{19}-C_{35} Aliphatics	N/A	**N/A**	**N/A**
C_{10}-C_{22} Aromatics	14.0[b]	**0.03**	**5012**

[a] RCNI = Relative Carbon Number Index
[b] fraction weighted toward lighter ends
* H = Henry's Law Constant (dimensionless)
** Koc = organic carbon partition coefficient (mL/g)

Dilution and Attenuation Factors

MCP Method 1 standards incorporate leaching concerns into the determination of soil cleanup standards via the use of Dilution and Attenuation Factors (DAFs), using the equation[2]:

$$DAF_{OHM} = [(6207)(H_{OHM})] + [(0.166)(Koc)] \quad \textbf{[6]}$$

where:

OHM = oil and/or hazardous material
H = Henry's Law Constant (atm-m^3/mol)
Koc = organic carbon partition coefficient (mL/g)

Expressing this relationship in terms of the dimensionless Henry's Law constant[3] yields the relationship:

$$DAF_{OHM} = [(150)(H_{OHM})] + [(0.166)(Koc)] \quad \textbf{[7]}$$

where:

H = Henry's Law Constant (dimensionless)

Based upon the H and Koc values proposed in Table 1, the DAFs calculated for the 6 hydrocarbon fractions of concern using equation **[7]** are presented in Table 2.

Table 2 - Proposed Dilution and Attenuation Factors (DAFs)

HYDROCARBON RANGE	TOX SURROG	RfD	**PROPOSEDD AF**
C_5-C_8 Aliphatics	n-Hexane	0.06	**8476**
C_9-C_{12} Aliphatics	n-Nonane	0.6	**3.5 EE 4**
C_9-C_{10} Aromatics	Pyrene	0.03	**345**
C_9-C_{18} Aliphatics	n-Nonane	0.6	**1.2 EE 5**
C_{19}-C_{35} Aliphatics	Eicosane	6.0	**N/A**
C_{10}-C_{22} Aromatics	Pyrene	0.03	**836**

Proposed MCP Method 1 Standards

MCP Method 1 leaching-based soil standards are calculated by use of the following equation:

$$[OHM]_{soil} = DAF_{OHM} \times [OHM]_{gw} \times C \quad \textbf{[8]}$$

where:

OHM_{soil} = leaching-based soil concentration (ug/g)
DAF = Dilution and Attenuation Factor (dimensionless)
OHM_{gw} = target groundwater concentration (ug/L)
C = 0.001 (conversion factor)

Using the fractional RfDs and DAFs presented in Table 2, the calculated Method 1 GW-1 and S-1 standards, **based solely on human health considerations,** are presented in Table 3.

Table 3 - Calculated Method 1 HUMAN HEALTH Standards

HYDROCARBON RANGE	**CALCULATED METHOD 1 VALUES**		
	GW-1, ug/L	**S-1, ug/g (Direct Contact)**	**S-1/GW-1, ug/g (Leaching)**
C_5-C_8 Aliphatics	**400**	**2000**	**3390**
C_9-C_{12} Aliphatics	**4000**	**2 EE 4**	**1.4 EE 5**
C_9-C_{10} Aromatics	**200**	**700**	**70**
C_9-C_{18} Aliphatics	**4000**	**2 EE 4**	**4.8 EE 5**
C_{19}-C_{35} Aliphatics	**40000**	**2 EE 5**	**N/A**
C_{10}-C_{22} Aromatics	**200**	**700**	**168**

Based upon the above, it appears that the two aromatic fractions will be controlled by leaching considerations for S-1/GW-1 soils: C_9-C_{10} Aromatics, and C_{10}-C_{22} Aromatics.

The calculation of S-1/GW-2, S-1/GW-3, and other soil cleanup values is predicated upon decisions that must be made on volatilization issues and aquatic impacts (discussed below).

(2) VOLATILIZATION CONCERNS/GW-2 STANDARDS

ISSUE: How should volatilization concerns be incorporated into the new VPH/EPH approach and cleanup numbers?

DISCUSSION: MCP Method 1 GW-2 groundwater standards are designed to be protective of exposures resulting from the volatilization of oil and hazardous materials (OHM) from the groundwater into an occupied building. The GW-2 groundwater standards are back-calculated from an acceptable indoor air concentration, using Henry's Law and an attenuation factor. The acceptable indoor air concentration is 20% of a Reference

Concentration (RfC) or the 50% odor recognition threshold, whichever is lower. The leaching/volatilization component of the S-1, S-2, and S-3/GW-2 soil standards are calculated by multiplying the GW-2 concentration by the compound/component-specific DAF.

As with leaching, the TPHCWG report found that volatilization is inversely related to molecular weight, and that distinct differences are noted between aliphatic and aromatic hydrocarbons. Once again, based upon the data presented, consolidation of the 11 fractions suggested by TPHCWG to the 6 fraction VPH/EPH range is recommended.

RfCs will need to be designated for each hydrocarbon fraction, based upon existing inhalation data and/or route-to-route extrapolation of oral RfD values.

Odor issues are more difficult to evaluate.

In general, straight-chain aliphatics have higher odor recognition thresholds (i.e., are less odorous) than aromatic compounds, with levels decreasing (i.e., becoming more odorous) with increasing molecular weight.[4] A double bond decreases the odor threshold, and functional groups can have a marked effect on odor recognition. Petroleum breakdown products and intermediaries, which are extremely variable and largely unknown, further complicate an assessment of this nature.

Limited data is available on odor thresholds for petroleum products. An odor threshold of 0.08 ppmv has been reported for #2 Fuel Oil[5], and 0.25 ppmv for gasoline[6]. Values for other petroleum products may be available via a literature search. While use of whole-product data is inconsistent with a component/surrogate approach, it at least provides real data which may be viewed as a "worst case" estimate of potential odor concerns.

RECOMMENDATION: Designate RfCs for the aliphatic and aromatic fractions, except C_{19} - C_{35} Aliphatics, which can be ruled-out as non-volatile. Calculate a GW-2 value using the fractional-average Henry's Law Constants presented in Table 1.

Because of the complexities involved, it is recommended that a surrogate odor threshold NOT be established based upon specific compounds or classes of compounds. Two options are recommended:

- Do not address odors, other than through the use of general ceiling levels; or

- Address odors using threshold odor recognition concentrations for whole products.

For the latter option, it is anticipated that health-based (RfC) concentrations will likely be a controlling factor for the C_5 - C_8 Aliphatics and C_9 - C_{10} Aromatics. However, the health-based value for the C_9 - C_{12} and C_9 - C_{18} Aliphatics may be relatively high. In these cases, the use of an 80 ppbv odor threshold may be advisable (based upon the reported odor threshold for #2 fuel oil of 0.08 ppmv). This would also be consistent with field experience which has shown that odor issues may be the controlling factor at some petroleum release sites, particularly #2 fuel oil in a residential setting.

(3) IMPACTS TO AQUATIC RECEPTORS/GW-3 STANDARDS

ISSUE: How should potential impacts to aquatic receptors be considered in the VPH/EPH approach and cleanup standards?

DISCUSSION: MCP Method 1 GW-3 standards are designed to be protective of aquatic organisms inhabiting a receiving surface water body impacted by a discharging groundwater plume. For each Method 1 chemical, the lowest available EPA Ambient Water Quality Criteria concentration is selected as the surface water concentration of concern. A ten-fold surface water/groundwater dilution factor is then assumed to back-calculate a groundwater concentration value of interest (GW-3 value).

Aliphatic and aromatic hydrocarbons are acutely toxic to aquatic organisms at concentrations that span 4 orders of magnitude. Within comparative carbon ranges, aromatic compounds are thought to be more toxic than aliphatic compounds. Based upon limited data, cyclic alkanes appear to be more toxic than normal or branched alkanes.[7]

In general, toxicity increases with increased molecular weight. For most low and mid-weight hydrocarbons, the toxic concentration in water falls between 20% and 70% of the compound's aqueous saturation concentration, irrespective of the compound's solubility limit. At increased molecular weights, however, toxicity levels are in excess of the compound's saturation limit. For PAH compounds, this transition point reportedly occurs around C_{16} (pyrene).[5]

According to a recent API publication, the median lethal concentrations (LC50) of crude oil and refined petroleum products range from 0.12 to 50.3 mg/L, with unleaded gasoline being the least toxic product, and unused crankcase oil being the most toxic product, as presented in Table 4.[5]

Table 4 - Whole Product Aquatic Toxicities

Product	Organism	LC50 (mg/L)	Reference
Diesel	Daphnia Magna	7.16	Maclean (1988)
Diesel	Salmo Gairdneri	2.52	Lockhart (1988)
#2 Fuel	Daphnia Magna	2.18	Maclean (1988)
Leaded Gasoline	Daphnia Magna	13.5	Maclean (1988)
Unleaded Gasoline	Salmo Gairdneri	5.40	Lockhart (1987)
Unleaded Gasoline	Daphnia Magna	50.3	Maclean (1988)
Crankcase Oil (new)	Daphnia Magna	0.38	Maclean (1988)
Crankcase Oil (used)	Daphnia Magna	4.87	Maclean (1988)

A draft UMass document prepared for MADEP in 1986 reported considerably higher values: for gasoline, a TLm (median Tolerance Level) of 90 mg/L (freshwater shad); for #2 fuel oil, a TLm of 200 mg/L (shad) and 20 mg/L
(saltwater rainbow trout eggs); and for #6 oil, a TLm of 2400 mg/L (shad).

While the above information provides an overall sense of the acute toxicity of petroleum products and hydrocarbons ranges, and upper limits for surface water quality criterion, the use of lethality endpoints is not appropriate in calculating Method 1 GW-3 groundwater standards. Accordingly, data on chronic effects levels for petroleum products is currently being researched by agency staff. If adequate information is not identified, an acceptable surface water concentration value could be set as a fraction of a whole-product lethality value, and/or on the basis of Ambient Water Quality Criteria for individual compounds. Data or recommendations in this regard are requested.

RECOMMENDATION: As with odor issues, the evaluation of aquatic impacts is not amenable to a fractional-surrogate approach based solely on an examination of individual compounds. Once again, consideration of whole-product toxicity data is advised.

As for specific aliphatic/aromatic fractions, the following is offered:

- **C_5 - C_8 and C_9 - C_{12} Aliphatics:** No recommendations are offered at this time; comments and recommendations are requested.

- **C_9 - C_{10} Aromatics:** Use of the benzene (700 ug/L) or ethylbenzene (430 ug/L) AWQC value is recommended as a surrogate value for this fraction. This would result in a GW-3 value of 4300 to 7000 ug/L for this fraction.

- **C_9 - C_{18} Aliphatics:** No recommendations are offered at this time; comments and recommendations are requested.

- **C_{19} - C_{35} Aliphatics:** Compounds in this range are essentially insoluble and immobile. Either a low value (e.g., 1 mg/L) or no value is recommended.

- **C_{10} - C_{22} Aromatics:** Use of a PAH ambient Water Quality Criteria (300 ug/L) is recommended as a surrogate value for this fraction. This would result in a GW-3 value of 3 mg/L.

Note that many of the Method 1 GW-3 criteria for hazardous materials are controlled by solubility limits (e.g., PAHs). The issue of apply ceiling limits to the above values are discussed below.

(4) FLOOR AND CEILING LEVELS

ISSUE: What modifications should be made to calculated (human) risk-based standards?

DISCUSSION: Generic "floor" and "ceiling" levels have been incorporated into all MCP Method 1 Standards. Floor levels applied to soil and groundwater standards include background concentrations and PQLs, to insure that all standards are reasonable and quantifiable. On the other extreme, no groundwater standard is set above 50% of its (single compound) water solubility limit, to insure that standards are truly reflective of dissolved conditions. Finally, a series of overall upper limits have been applied to both soil and groundwater standards, in an attempt to address aesthetic, organoleptic, phytotoxicity and odor concerns not otherwise considered in the development of the Method 1 standards.

Relative to the VPH and EPH fractions, PQL values associated with the proposed VPH and EPH analytical methods are likely to be well below any risk-based cleanup standard. Similarly, risk-based cleanup levels are likely to be well above natural and anthropogenic background concentrations of these fractions.

Conversely, it is possible that calculated health-based cleanup values for aliphatic fractions in soil could exceed their theoretical saturation concentrations, determined through the use of partitioning models. In such cases, the contaminants of concern would be present as "free liquids" within the soil matrix.

RECOMMENDATION: PQLs and background considerations are not deemed to be an issue for the VPH and EPH fractions, and need not be further considered, unless decisions made on solubility "floor" levels lower a groundwater standard to a concentration below the (likely) analytical PQL. Of greater concern are solubility limits and overall ceiling limits, discussed in more detail below.

With respect to soil, it is recommended that all Method 1 standards be set no higher than a predicted saturation concentration for sandy soils, to insure that "free liquids" are not present. However, the agency is seeking comment on whether free liquids should be allowed under a Method 2 or 3 Risk Characterization method.

(5) SOLUBILITY ISSUES/CEILING VALUES

ISSUE: Should any of the calculated risk-based Method 1 VPH/EPH cleanup standards be capped based upon solubility?

DISCUSSION: Gasoline is by far the most soluble petroleum product, with solubility values reported up to 240 mg/L.[4] BTEX compounds and MTBE, however, represent up to 90% of the total water soluble fraction of gasoline. The solubility of #2 fuel oil has been reported to be in the range of 2-6 mg/L, with BTEX compounds comprising 30 - 50% or more of the water soluble fraction.[5,8] Jet fuel and kerosene are also only sparingly soluble in water, in the range of #2 fuel oils, with BTEX, naphthalene, and akyl-naphthalenes comprising the majority of the water-soluble fraction. Crankcase oil is even less soluble at less than 1 mg/L.[5]

TPHCWG has proposed a set of equations relating the solubility of a compound or hydrocarbon fraction to its Relative Carbon Number Index:

$\log_{10}S = [-0.55][RCNI] + 4.6$	(aliphatics, $R^2 = 0.94$)	**[9]**
$\log_{10}S = [-0.21][RCNI] + 3.7$	(aromatics, $R^2 = 0.89$)	**[10]**

where:

S = Solubility (mg/L)
RCNI = Relative Carbon Number Index

Based upon these equations, and the list of compound properties provided by TPHCWG, a tabulation of the solubility of compounds within the 6 VPH/EPH hydrocarbon fractions is presented in Table 5.

Table 5 - Aqueous Solubilities of VPH/EPH Fractions

HYDROCARBON RANGE	AQUEOUS SOLUBILITY OF COMPOUNDS (MG/L)			
	HIGH VALUE	LOW VALUE	CALC AVG RANGE VALUE	
			RCNI[a]	VALUE
C_5 - C_8 Aliphatics	535	9.5	6.5	11
C_9 - C_{12} Aliphatics	1.8	0.004	10.5	0.07
C_9 - C_{10} Aromatics	100	3.5	9.5	51
C_9 - C_{18} Aliphatics	1.8	3.11 EE -7	12.0[b]	0.01
C_{19} - C_{35} Aliphatics	N/A	N/A	N/A	N/A
C_{10} - C_{22} Aromatics	100	2.6 EE -4	14.0[b]	5.8

[a] RCNI = Relative Carbon Number Index
[b] weighted toward more soluble (lighter) ends

Two notes/caveats on this tabulation:

o The presence of double or triple bonds within a carbon range substantially increases solubility, as does ring formations and branching.[2] Some of the alkenes and alkynes present within the VPH/EPH fractions have high solubilities, which tends to elevate the average range value presented in Table 5. This is a little misleading, however, due to the low levels of such compounds present in most fuel products.

o The average solubility values within the (consolidated) fractions are also a little misleading, as solubility values drop substantially with increasing molecular weight. Note that aliphatic compounds greater than C_{12} are essentially insoluble (i.e., saturation levels less than 1 ug/L).

RECOMMENDATION: Similar to odor and aquatic impact concerns, consideration of whole-product solubility, as well as compound/fraction-specific solubility data, is advised.

It is difficult, and not entirely meaningful, to estimate solubility limits for VPH/EPH fractions. Based upon recommendations made earlier on Method 1 cleanup standards, however, the health-based GW-1 standard for C_{19} - C_{35} Aliphatics (40 mg/L) would clearly exceed solubility limits within this range. Recommended GW-3 values for the C_5 - C_8, C_9 - C_{12}, and C_9 - C_{18} Aliphatic fractions are also pushing the boundaries of likely solubility limits for these ranges, although such levels are not clearly in excess of what might reasonably be expected at some sites.

For these reasons, the following recommendations are made:

- The GW-1 and GW-3 value for C_{19}-C_{35} Aliphatics should be capped at 1 mg/L. Values in excess of this level are likely indicative of non-dissolved conditions, and/or anomalous conditions not amenable to the Method 1 risk assessment process.

- GW standards for other fractions should not be capped. While it is unlikely that risk-based standards would be approached at most sites, there is enough uncertainty present to refrain from imposing solubility limit ceilings.

(6) OVERALL CEILING LEVELS/SOIL ODOR ISSUES

ISSUE: What overall ceiling values should be applied to soil and groundwater Method 1 standards, to address aesthetic, organoleptic, phytotoxicity and odor concerns?

DISCUSSION: MCP Method 1 GW standards have an overall ceiling of 50 mg/L. Method 1 soil standards have an overall ceiling value ranging from 100 ug/g to 5000 ug/g, based upon soil category (i.e., S-1, S-2, or S-3), and the OHM's vapor pressure and Odor Index.

None of the GW standards proposed in this paper are in excess of 50 mg/L, although some of the GW-2 standards may be. In such cases, they would be capped at 50 mg/L.

Although there is no shortage of anecdotal reports on odor conditions, well-documented field data/studies are rare, with the Natick UST project perhaps being the best available data in this regard. As part of this effort, odor observations were recorded for over 200 soil samples obtained during UST removal operations, for comparison with TPH concentrations. Although little overall correlation was noted, it is interesting to note that all but 2 soil samples containing TPH concentration greater than 500 ug/g TPH had at least a slight odor noted, and the majority of soil samples containing greater than 1000 ug/g TPH were characterized as possessing moderate or heavy odors.[9]

Clearly, some of the risk-based soil cleanup values for the VPH/EPH fractions may be at levels at which an odor could be present. Unfortunately, given the complexities associated with petroleum odors, it is virtually impossible to predict with any degree of certainty soil concentrations at which odors will be discernable.

Given this uncertainty, and given the economic ramifications of lowered cleanup standards, a decision needs to be made on how the agency should incorporate odor concerns into the calculation of Method 1 standards. Good arguments can be offered on both sides of this issue:

- While Method 1 standards do not apply at sites where air impacts (e.g., odors) are known to exists, soils containing VPH/EPH levels below

Reportable Concentrations are unregulated materials, and as such are likely to be indiscriminately transported and reused. Thus, soils at depth that were not an odor problem at their point of excavation could be reused at residential properties, during which an odor problem may be encountered by concerned homeowners. In such cases, the odor itself is not the primary problem, it's more the concern over what "chemicals" could be present in the soil. This could lead to expensive testing (often by MADEP) and unnecessary anxiety.

- Conversely, based upon anecdotal experiences, most petroleum odors in soil quickly dissipate to non detectable levels, once the soil is excavated and exposed to the atmosphere. Given the ephemeral nature of this concern, and the ambiguities involved, is it appropriate to impose cleanup levels that are more stringent than risk-based values? Such values will not only lead to more expensive remedial measures, but will also increase required filings of Activity and Use Limitations (AULs).

Although it is not possible to determine an Odor Index for the various aliphatic and aromatic ranges, in accordance with the existing Method 1 standard developmental criteria, ceiling values could be determined on the basis of the average vapor pressures within the various VPH/EPH fractions.
Based upon an evaluation conducted by TPHCWG, a compound's vapor pressure is directly related to its Relative Carbon Number Index (RCNI), regardless of whether that compound is an aliphatic or aromatic hydrocarbon. According to TPHCWG, the following relationships exist in this regard:

$$\log_{10}VP = [-0.52][RCNI] + 2.4, \text{ for } RCNI \leq 12 \quad (R^2 = 0.96) \qquad \textbf{[11]}$$

$$\log_{10}VP = [-0.37][RCNI] + 0.68, \text{ for } RCNI > 12 \quad (R^2 = 0.99) \qquad \textbf{[12]}$$

where:

VP = Vapor Pressure (atm)
RCNI = Relative Carbon Number Index

Based upon these equations, and the list of compound properties provided by TPHCWG, a tabulation of the vapor pressures of compounds within the 6 VPH/EPH hydrocarbon fractions is presented in Table 6.

On the basis of (average) vapor pressure, and in accordance with the existing Method 1 development criteria[2], the values for all VPH fractions (i.e., C_5 - C_8 Aliphatics, C_9 - C_{12} Aliphatics, and C_9 - C_{10} Aromatics) would be capped as follows: S-1 @ 100 ug/g; S-2 @ 500 ug/g, and S-3 @ 500 ug/g. This would likely lower several of the S-1 risk-based values.

Table 6 - Vapor Pressures of VPH/EPH Fractions

HYDROCARBON RANGE	VAPOR PRESSURE OF COMPOUNDS (atm)			
	HIGH VALUE	LOW VALUE	CALCULATED AVG RANGE VALUE	
			RCNI[a]	VALUE
C_5 - C_8 Aliphatics	1.7	0.06	6.5	0.10
C_9 - C_{12} Aliphatics	0.02	1.6 EE -4	10.5	8.7 EE -4
C_9 - C_{10} Aromatics	6.1 EE -3	3.5 EE -4	9.5	2.9 EE -3
C_9 - C_{18} Aliphatics	0.02	2.2 EE -7	12.0[b]	1.4 EE -4
C_{19} - C_{35} Aliphatics	N/A	N/A	N/A	N/A
C_{10} - C_{22} Aromatics	2.7 EE -3	4.1 EE -11	14.0[b]	3.2 EE -5

[a] RCNI = Relative Carbon Number Index
[b] weighted toward more volatile (lighter) ends

For the EPH fractions, assuming the lowest Odor Index (i.e., least odor condition), each hydrocarbon range would be capped as follows: S-1 @1000 ug/g, S-2 @ 2500 ug/g, and S-3 @ 5000 ug/g.

RECOMMENDATION: With one exception, it is recommended that soil ceiling levels be established at the levels already specified in the Method 1 process. The exception is to raise the ceiling for C_{19} - C_{35} Aliphatics, which are essentially insoluble, non-volatile, and immobile hydrocarbons. The recommended caps are presented in Table 7.

Based upon the above recommendations, the following may be expected:

- Method 1 standards at gasoline release sites will be predominantly controlled by ceiling values. While some of the risk-based values for the VPH fractions are expected to be lower than the ceiling levels listed above (e.g., S-1/GW-1 for C_9- C_{10} Aromatics at 70 ug/g), most S/GW values will be capped well below health-based values.

  However, it is noted that VPH hydrocarbons are relatively

Table 7 - Recommended Soil Ceiling Values

HYDROCARBON RANGE	RECOMMENDED SOIL CEILING CONCENTRATIONS (UG/G)		
	S-1	**S-2**	**S-3**
C_5 - C_8 Aliphatics	100	500	500
C_9 - C_{12} Aliphatics	100	500	500
C_9 - C_{10} Aromatics	100	500	500
C_9 - C_{18} Aliphatics	1000	2500	5000
C_{19} - C_{35} Aliphatics	2500	5000	5000
C_{10} - C_{22} Aromatics	1000	2500	5000

volatile and odorous, and even with the proposed ceiling values, most gas station sites (where contamination is limited to S-2 and S-3 soils) will still qualify for a Class A or B RAO with levels of gasoline hydrocarbons in excess of 1000 ug/g, a value substantially above what many other states currently allow.

- Method 1 standards at #2 fuel oil release sites will also be controlled, by in large, by the ceiling values. However, given the typical breakdown of hydrocarbon classes at such sites (i.e., typical distribution of hydrocarbons between C_9 - C_{18} Aliphatics, C_{19} - C_{35} Aliphatics, and C_{10} - C_{22} Aromatics), and that three hydrocarbon fractions will be replacing a single "TPH" standard, the total level of hydrocarbons that can be left in soil for a Class A-2 or B-2 ("residential") RAO will increase from the current value of 500 ug/g to levels between 1000 and 3000 ug/g, dependent upon the specific aromatic/aliphatic content of the soil "TPH".

As a final point of consideration, note two factors in assuaging concerns arising from the use of these ceiling factors:

* The Method 1 cleanup standards are based upon the average concentration in the soil, and thus some soil samples can be above the stated values; and

* Parties always have the option to undertake a Method 3 risk assessment at sites where they believe the Method 1 ceiling levels are inappropriate (MADEP guidance in this regard would be advisable).

(7) UPPER CONCENTRATION LIMITS (UCLs)

ISSUE: What should the UCLs be for the various or collective VPH/EPH fractions?

DISCUSSION: Upper Concentration Limits are "gross" contamination levels that cannot be left at a site and still be called a permanent solution. Roughly based upon toxicity and fate/transport considerations, UCLs are a recognition that, given uncertainties in current toxicity information, and future exposure pathways, it is imprudent public policy to allow extremely high concentrations of oil or hazardous materials to remain at sites considered to be "permanently" cleaned up.

UCLs are set at 10 times the highest Method 1 soil and groundwater standard, capped at 100 mg/L in groundwater, and 10,000 ug/g soil. Currently, the UCL for "TPH" is listed as 100 mg/L in groundwater, and 10,000 ug/g in soil. At issue is how the UCL should be set for the VPH/EPH fractions.

Given the limited solubility of petroleum products, few (if any) sites have or will exceed the current groundwater UCL of 100 mg/L of TPH. However, the current soil UCL of 10,000 ug/g TPH has been problematic at a number of sites, and a case can be made that this ceiling is unreasonable and unnecessary:

- Residual saturation levels in the vadose zone for middle and heavy distillates can be as high as 39,000 ug/g in fine sands and silts.[10] Concentrations approaching residual saturation levels are not uncommon, particularly at sites with a history of NAPL conditions. While gasoline and other light distillates are amenable to recovery by pump and treat and/or SVE systems, heavier products, such as #6 Fuel Oil, are very difficult to recover from a formation, except through excavation. In many cases, excavation projects are limited by the presence of buildings or subsurface structures or utilities.

- The heavier aliphatic hydrocarbons posses a relatively low toxicity. Direct-contact S-1 (residential) values for C_9 - C_{18} Aliphatics have been previously estimated at 20,000 ug/g; C_{19} - C_{35} Aliphatics estimated at 200,000 ug/g. Note that in most cases, these compounds constitute more than 50% of diesel/#2 fuel oil hydrocarbons.

- Petroleum hydrocarbons are in general quite biodegradable, particularly the light and mid-weight aliphatic fractions. While the heavier aliphatic fraction (i.e., greater than C_{19}) is more resistant to biodegradation, it is also essentially insoluble, non-volatile, immobile, and relatively non-toxic.

Conversely, there are some reasons not to raise the recommended UCL values:

- Substantial staining and/or odors are likely to be present in soils containing greater than 10,000 ug/g (1%) petroleum hydrocarbons.

- There is evidence that concentrations of petroleum hydrocarbons in soil in excess of 10,000 ug/g may result in phytotoxic impacts to plant seed germination.[11]

RECOMMENDATION: It is recommended that the effective UCL levels for petroleum contaminated soils be elevated, by the apportionment of UCL values among the VPH/EPH fractions, considering the toxicities and fate characteristics of each fraction. Recommended values are proposed in Table 8.

Table 8 - Recommended UCL Values

HYDROCARBON RANGE	PROPOSED UCL	
	SOIL (UG/G)	G.W. (MG/L)
C_5 - C_8 Aliphatics	5000	100
C_9 - C_{12} Aliphatics	5000	100
C_9 - C_{10} Aromatics	5000	100
C_9 - C_{18} Aliphatics	20,000	100
C_{19} - C_{35} Aliphatics	20,000	100
C_{10} - C_{22} Aromatics	10,000	100

Note that all values in Table 8 are consistent with the current MCP approach (i.e., 10 times the soil ceiling levels recommended in Table 7 or 10,000 ug/g; groundwater ceiling of 100 mg/L) except for the C_9 - C_{18} and C_{19} -C_{35} Aliphatics, which have been raised to 20,000 ug/g.

(8) VPH/EPH CLEANUP STANDARDS

ISSUE: How should VPH, EPH, and/or TPH Method 1 cleanup standards be articulated?

DISCUSSION: At present, the MCP has a designated Method 1 standard for "TPH", defined as > C_{10} hydrocarbons. There is currently no collective hydrocarbon standard for VPH-range hydrocarbons.

The draft VPH/EPH analytical methods have proposed a "toxicity weighted" VPH, EPH, and TPH standard, where each fraction is weighted according to its (human) toxicity to produce a single VPH, EPH, and/or TPH value. Based upon the leaching, odor, and ceiling considerations discussed previously in this paper, however, it has become clear that human toxicity values will not be the controlling factor in the designation of many of the soil and groundwater fractional standards. For this reason, it does not appear possible to have a consolidated "weighted" VPH, EPH, or TPH Method 1 standard.

RECOMMENDATION: Set individual Method 1 soil and groundwater standards for each of the 6 VPH/EPH hydrocarbon range fractions. It may be advisable to retain a "TPH" term and definition in the MCP, however, as that term may still have relevance to certain program and regulatory items, such as Remediation Wastes. It may also be advisable to change the current definition of TPH, so that it defined as the sum of VPH and EPH values.

(9) VPH/EPH REPORTABLE CONCENTRATIONS

ISSUE: How will the new VPH/EPH standards effect Reportable Concentration parameters and values in the MCP?

DISCUSSION: Similar to the current Method 1 Cleanup Standards, the MCP presently has a Reportable Concentration for "TPH". There are 3 options available to integrate the new VPH/EPH approach into this area:

- Make no changes; maintain a "TPH" Reportable Concentration and do not add in fractional VPH/EPH Reportable Concentrations. This would allow the use of existing (and less expensive) analytical methods, and would have the effect of casting a "broad net" for fuel oil release sites, as the EPH standards are less conservative than the current TPH standard. The new EPH approach, standards, and analytical methodology would then be used to get a site out of the system. A significant disadvantage here, however, is that VPH range contaminants will not be brought into the system, as the current TPH definition only includes C_{10} and heavier hydrocarbons.

- Add in fractional VPH and EPH Reportable Concentrations, and maintain the existing TPH Reportable Concentration. This would cast the broadest possible notification net, and would not require parties to use the more expensive VPH/EPH analytical methodologies to determine reporting obligations.

- Add in fractional VPH and EPH Reportable Concentrations, and delete the existing TPH Reportable Concentration. This would make the Reportable Concentrations more consistent with the Method 1 Cleanup Standards.

RECOMMENDATION: Add fractional VPH and EPH Reportable Concentrations, and eliminate the existing TPH Reportable Concentration. The Reportable Concentrations for the 6 VPH/EPH fractions can be selected from the Method 1 Cleanup Standards using the approach and hierarchy indicated in Appendix E of the MCP Numerical Standards background document[2].

Failure to establish fractional VPH Reportable Concentrations (i.e. C_5-C_8 Aliphatics, C_9-C_{12} Aliphatics, and C_9- C_{10} Aromatics) would not be protective, as these contaminants are currently not addressed in the MCP. While there is some concern that increased analytical expenses would be incurred in using the new VPH/EPH analytical methods, it is believed that most in the regulated community would find this a preferable option, in exchange for narrowing the notification net. Moreover, through guidance, MADEP can recommend analytical screening techniques to minimize the need to perform the more expensive VPH/EPH methods. (See Application and Program Issue #5)

(10) REQUIRED REGULATORY ACTIONS/REVISIONS

ISSUE: What MCP revisions, if any, will be needed to implement the new VPH/EPH approach?

DISCUSSION: Several options are available:

- Promulgate the aliphatic/aromatic standards as Method 2 cleanup standards, as specified in the MCP at 40.0982(7). This could be done through policy, without regulatory change. A limitation with this approach is the failure to address Reportable Concentrations, and to mandate the use of VPH standards at gasoline release sites.

- Revise the MCP:

  - **Subpart A -** VPH, EPH, and each hydrocarbon fraction would require definition; the TPH definition should also be modified.

  - **Subpart C -** Slight change required in 40.0360 relative to Reportable Concentrations for petroleum hydrocarbons.

  - **Subpart I -** Changes would be required in Subpart I to eliminate the current TPH Method 1 standards, and designate 6 new standards for the VPH/EPH fractions. Similar changes would be required in the UCL tables.

  - **Subpart O -** The Numerical Ranking System criteria in Subpart O would require evaluation to determine if changes are appropriate.

  - **Subpart P -** Changes would be required for the Reportable Concentrations listed on the MOHML: delete TPH, and add in values for 6 VPH/EPH fractions.

RECOMMENDATION: Both options are recommended. In order to allow the regulated community the opportunity of using the new methods as soon as possible, the VPH/EPH standards should be issued as Method 2 Cleanup Standards. Subsequently, MADEP can begin the process to revise the MCP to reflect the recommended changes.

APPLICATION AND PROGRAM ISSUES

Beyond the derivation of Method 1 Cleanup Standards, a number of additional issues exist on the use, application, interpretation, and implications of the new VPH/EPH approach.

(1) USE OF VPH vs EPH

ISSUE: When is it necessary to test a sample for VPH? For EPH? For both?

DISCUSSION: The VPH method covers C_5 - C_{12} hydrocarbons; the EPH method covers C_9 - C_{35} hydrocarbons. Most petroleum products contain hydrocarbons within both ranges, to varying degrees. To ensure that all hydrocarbons are accounted for in every sample, it would be necessary to test for both VPH and EPH. However, this increases costs.

The two most commonly released petroleum products in Massachusetts are gasoline and diesel/#2 fuel oil. Greater than 90% of gasoline hydrocarbons should be less than C_{12}, and thus detectable by the VPH method. Similarly, greater than 80% of diesel/#2 fuel oil hydrocarbons should be heavier than C_9, and thus detectable by the EPH method.

Heavier fuel oils will be almost exclusively in the EPH range. While unused crankcase (lubricating) oil will contain hydrocarbons mainly in the EPH range, used crankcase oil can contain significant concentrations of VOCs (due to leaky cylinder rings in internal combustion engines and/or contamination with chlorinated solvents during storage). Although additional data is needed, mineral oils and dielectric oils would appear to be exclusively within the EPH range. Similarly, while additional compositional information would be desirable, Jet Fuels and Kerosene would appear to contain hydrocarbons mostly in the EPH range, though significant concentrations may also be present in the heavier VPH range.

RECOMMENDATION: For samples known to be contaminated ONLY with the designated petroleum product(s), testing recommendations are presented in Table 9:

Table 9 - Recommended Testing Procedures

PETROLEUM PRODUCT	VPH	EPH
Gasoline	X	
Fresh Diesel/#2 Fuel Oil[a]	X	X
Weathered Diesel/#2 Fuel Oil[a]		X
#3 - #6 Fuel Oils		X
Waste (Crankcase) Oil	X	X
Jet Fuel/Kerosene	X	X
Mineral/Dielectric Oils		X
Unknown Oils/Sources	X	X

[a] Samples with a headspace VOC screening level > 100 ppmv to be considered "fresh"

(2) BTEX TESTING AT DIESEL/#2 FUEL OIL SITES

ISSUE: Is it necessary to look for BTEX compounds at sites contaminated ONLY by a release of diesel/#2 fuel oil?

DISCUSSION: In Issue #1, a recommendation is made to require VPH testing at fresh diesel/#2 fuel oil release sites, but not weathered release sites. A secondary issue involves the necessity to test for BTEX compounds in such cases.

While BTEX compounds are in fact present in diesel/fuel oils, they are usually present only in low concentrations. Of the 84 BTEX samples obtained during the Natick Project, no exceedances were observed in any soil sample, using Method 1, S-1/GW-1 standards.[9] This is consistent with MADEP experiences at other sites of this nature.

However, there is now compelling evidence which indicates that traditional soil sampling methods can grossly under-report VOC levels (see Issue #4 below), so BTEX data generated from the Natick study, and all past BTEX soil sampling data, must be considered suspect.

RECOMMENDATION: Similar to the recommendation made in Issue #1 above, BTEX analysis of soil samples is not recommended at sites contaminated ONLY by a release of <u>weathered</u> diesel/#2 fuel oils. However, until further data is generated on BTEX presence in unweathered samples, analysis for BTEX compounds is recommended for "fresh" diesel/#2 fuel oil contaminated soil samples. Sampling of the groundwater for BTEX compounds should be determined on a case-by-case basis, based upon the sensitivity of potential pollutant receptors.

(3) PAH TESTING AT DIESEL/#2 FUEL OIL SITES

ISSUE: Is it necessary to look for PAH compounds at sites contaminated ONLY by a release of Diesel/#2 Fuel Oil?

DISCUSSION: Many consultants and LSPs have historically avoided looking for PAH compounds at fuel oil contaminated sites, partially due to the expense of testing, partially worried about what they may find. MADEP has generally not pursued this omission, due to the fact that if the conventional TPH Method 1 cleanup standard of 500 ug/g is reached, in most cases, exceedance of a PAH Method 1 Standard would not be likely (as supported by the Natick UST Project data).

However, as the new (EPH) approach will allow much higher hydrocarbon cleanup levels, PAH compounds are more important, and, in many cases, may be the limiting/controlling factor for a site cleanup. Two compounds are particularly problematic, due to their concentrations in fuel oil, and the relatively low MCP Method 1 S-1/GW-1 cleanup standards: naphthalene (4.0 ug/g), and 2-methylnaphthalene (0.7 ug/g). However, note that the Method 1 standards for both of these compounds are controlled by leaching considerations, not direct contact. The (S-1) direct contact values are considerably higher: 100 ug/g naphthalene and 1000 ug/g 2-methylnaphthalene.

Of 29 soil samples analyzed for PAHs during the Natick Project, 6 exceeded the S-1/GW-1 naphthalene standard, and 11 exceeded the S-1/GW-1 2-methylnaphthalene standard. Of 6 samples containing TPH concentrations less than 500 ug/g, however, no sample exceeded the naphthalene standard, and only 1 of 6 samples (slightly) exceeded the 2-methylnaphthalene standard.

RECOMMENDATION: Unless the total (unadjusted) TPH concentration is less than 500 ug/g, PAH testing of soil should be undertaken, at least for naphthalene and 2-methylnaphthalene. Where these standards are exceeded, however, it is recommended that a Method 2 Risk Characterization approach be utilized, to address leaching concerns at the site in question. In many cases, it is likely that a compelling case can be readily made that leaching is not occurring, and an alternative standard can be justified. MADEP guidance in this regard is recommended.

It is further recommended that a reduced list of targeted PAH compounds be developed for sites contaminated with diesel/#2 fuel oil, due to the relatively low levels of heavier (4 - 5 ring) PAH compounds present in such products. This effort would also address analytical difficulties associated with the detection of very low concentrations of carcinogenic PAHs in groundwater, at least for these types of sites.

(4) REQUIRED USE OF METHANOL PRESERVATIVE FOR VPH SAMPLES

ISSUE: Should field preservation of VPH soil samples with methanol be required?

DISCUSSION: The proposed VPH analytical method requires the addition of methanol to sample vials prior to or at the time of field sampling. Virtually every commentor has objected to this provision, based upon logistical difficulties. However, no commentor challenged the basis for this recommendation, and most declined to offer an acceptable alternative. This is probably the most controversial element in the proposed VPH/EPH methods.

Existing methods for the collection of soil samples for VOC/BTEX analysis involve filling a standard 40 or 60 mL VOA vial, and applying a teflon-lined septum screw cap. The samples are cooled, delivered to a laboratory, and analyzed within 14 days of collection (note that "within" 14 days of collection usually translates to analysis near or on the 14th day).

There is a growing body of evidence indicating that existing sampling and storage procedures can substantially under-report VOC soil concentrations in collected samples. Three mechanisms are to blame: (1) initial sampling and sub-sampling activities that disturb/destroy soil structure and/or aerate samples, (2) volatilization/diffusion out of the sample container during storage, and (3) biodegradation of contaminants during storage.

In vadose-zone soil samples obtained outside the release location, contamination occurs via vapor-phase diffusion from the source area. In such cases, mass transfer is occurring from the vapor phase to the soil moisture and soil solids, and a significant percentage of total contaminant levels are present in the vapor phase. In such cases, common sampling techniques (e.g., trowel transfer to a container) destroy the soil structure, aerate the soil, and liberate soil gases to the ambient air. Such losses are less pronounced in silty/clayey soils, which tend to retain some of their soil structure even with invasive sampling procedures. Initial sampling losses are less problematic in source areas, where about 70 - 90+% of the contaminant mass is sorbed onto the soil solids and dissolved in the soil moisture.

In the hours and days following sample collection, volatilization losses continue to occur, where VOCs partition from the soil, and diffuse through or around the threaded vial cap. This is especially true in cases where soil grains entrained on the vial screw threads prevent a tight seal. After a few days, biodegradation may become the predominant loss mechanism. Combined losses occurring in this manner can be up to, or greater than, an order of magnitude.

While the degree and implications of sampling and storage losses appear to be significant, there has not been a great deal of research or publicity on this topic. Based upon a limited number of inquiries, 14 reference papers and documents have been identified on this subject. A list of these publications is appended as Attachment A. Most of these papers have been written in the last few years, and many have not (yet) appeared in peer-reviewed journals. Some are not even published. A few of the more notable efforts are discussed below.

- In a comprehensive study partially funded by the state of Wisconsin, levels of Gasoline Range Organics (similar to VPH) decreased up to 70% after unpreserved storage for 14 days at 4 degrees C. Losses of more volatile components like benzene were even more pronounced at 90%. As one would expect, losses were more significant in sandy soils than in silty/clayey soils. In contrast to these results, soil samples preserved in methanol were found to remain at a stable concentration for at least 28 days.[12]

- Studies conducted at the U.S. Army Cold Regions Research and Engineering Laboratory in Hanover, New Hampshire indicate substantial losses of VOCs using conventional sampling and storage procedures, including losses of 90% or more of benzene from soils stored in a VOA vial at 4 degrees C for 14 days. Conversely, soil samples preserved in methanol and stored at room temperature were found to remain at a stable concentration for 42 days.[13]

- In a peer-reviewed article published in Environmental Science and Technology, soil samples stored without methanol preservation were found to contain up to 81% less VOCs than split samples stored in methanol. Volatilization was postulated to be the primary loss vehicle.[14]

- In a limited evaluation conducted by MADEP in August and September 1995, duplicate soil samples were obtain from three split-spoon samples and 2 excavation samples at a site in Natick contaminated by chlorinated solvents. In each duplicate pair, one sample was collected and stored in the conventional manner (i.e., a completely filled 40 ml VOA vial with teflon-lined screw cap). The other sample was collected per the proposed VPH method (i.e., methanol preserved in the field at time of collection). The results are presented in Table 10.[15]

As indicated in Table 10, losses for PCE ranged from 1 to 3 orders of magnitude Moreover, note that the contaminant in this study was a chlorinated solvent resistant to short-term biodegradation, indicating most of the observed losses were likely due to volatilization mechanisms.

Table 10 - MADEP Methanol Preservation Study

SAMPLE ID	TYPE SOIL	HOLDING TIME	PCE SOIL CONC (UG/KG)	
			W/ MEOH	W/O MEOH
103D-S-03	Sand	11 Days	550	2
103D-S-09	Sand	7 Days	220	10
106D-S-04	Sand	9 Days	2100	340
UST Bottom	Sand	13 Days	11,000	810
UST West	Sand	13 Days	490,000	380

The primary objections and limitations to field preservation with methanol involve logistical concerns. These include: (1) health and safety concerns, (2) added complexity, and (3) DOT shipping regulations. Of these concerns, the DOT shipping issue is perhaps the most problematic, in that shipments of methanol are subject to regulation by DOT as a hazardous material under Title 49 of the Code of Federal Regulations (CFR). However, the minor amounts of methanol proposed in the VPH method would be subject to the small quantity exemption provisions of 49 CFR 173.4, which substantially reduces (but does not eliminate) regulatory requirements and paperwork.

It should be noted that some alternatives to the field use of methanol exist, and research on additional methods is underway. For example, Wisconsin allows the use of a field sampling device that can obtain and seal an undisturbed sample of soil. The sample is then shipped to a laboratory, where methanol must be added within 48 hours of sampling. Other researchers are looking into the use of other solvents, or dilute solutions of methanol (which would avoid DOT regulation).

Finally, it should be noted that Alaska, New Mexico, Minnesota, and Wisconsin have reportedly adopted the methanol preservation requirement, and a number of additional states, including Arizona, Maine, and New Jersey are reportedly considering such a requirement.

RECOMMENDATION: The issue of VOC losses during conventional VOA sampling and storage procedures simply cannot be ignored. Nevertheless, the logistical issues involved in using methanol in the field are not trivial.

Two recommendations are offered:

- o Similar to Wisconsin, the use of sealed-tube samplers should be allowed as an alternative to field preservation, provided methanol is added within 48 hours of sampling.

- o LSPs can use RAPS to develop alternative sampling and preservation techniques, such as dilute methanol, as long as the validity of such techniques can be substantiated.

(5) USE OF OLD/NEW "TPH" DATA

ISSUE: Should the "retrofitting" of old TPH data, or use of new TPH data, be allowed? If so, what assumptions on aliphatic/aromatic fractions would be appropriate?

DISCUSSION: There are numerous sites for which "TPH" concentrations have been determined, and for which there is considerable interest to apply the new VPH/EPH risk assessment approach. In such cases, it is obviously preferable to use existing data, as opposed to conducting extensive new analyses by the VPH/EPH methods. Similarly, for future efforts, it would be cost-effective to be able to use relatively inexpensive "screening" methods to quantitate some sort of a "TPH" parameter, if it were possible to correlate that data to a VPH/EPH value. In both cases, correlations would be contingent on an assumed distribution of aliphatic and aromatic compounds that comprise the "TPH" concentration.

Note that at present this is primarily an issue for heavier molecular weight products, not gasoline, given the common use of "TPH" screening methods for C_9 and greater hydrocarbons. However, given the recent development of innovative screening techniques for gasoline-range organics, and proposed establishment of C_5 - C_{12} cleanup standards, interest in this area is only a matter of time.

Any correlation allowed or recommended by MADEP in this regard would have to be conservative, in order to be protective in most situations. At issue is the degree of conservatism.

The typical breakdown of aliphatic/aromatic compounds in common petroleum products is presented in Table 11.[4,5,6]

Table 11 - Typical Composition of Petroleum Products

PRODUCT	CARBON RANGE	PERCENT ALIPHATIC	PERCENT AROMATIC
Gasoline	C_4 - C_{12}	35% - 80%	10% - 40%[a]
#2/Diesel Oil	C_8 - C_{21}	60% - 70%	30% - 40%
#3-#6 Fuel Oil	C_8 - C_{30} +	20% - 50%	30% - 40+ %
Used Crankcase Oil	C_{15} - C_{50} +	50% - 90%	10% - 30%
Jet Fuel/Kerosene	C_9 - C_{16}	60% - 80%	5% - 20%
Dielectric Oils	C_{12} - C_{22} (?)	?	?

[a] includes BTEX compounds

In reviewing Table 11, it is important to note the following:

- The composition of petroleum products is highly variable, and the aromatic content of any given petroleum product could be higher than indicated for "typical" products.

- At present, there is still insufficient data available on the composition of petroleum products, and what is available is not always consistent.

- The aromatic fraction of weathered petroleum residuals are likely to be higher than virgin products, as aromatic compounds are typically more resistant to biodegradation.

To date, some limited VPH/EPH testing results have been received. Based upon an evaluation of this data, the aromatic content of most EPH samples has been less than 30% of the total petroleum hydrocarbon concentration. Although the identity of the petroleum product released is not always known or indicated, it appears that most EPH analyses have been done for diesel/#2 fuel oil samples. Available VPH data is more limited, and no conclusion may be drawn at this point in time.

RECOMMENDATION: It is recommended that the use of old and new "TPH" data be allowed, under the following conditions:

o LSPs must use RAPS in determining when it is appropriate to use TPH data in determining aliphatic and aromatic fractions. Factors to consider include: (1) knowledge of released petroleum product(s); (2) the reliability, validity, and bias of the TPH analytical method; and (3) sensitivity of site and potential pollutant receptors.

o For gasoline data, the recommended default compositional (non BTEX/MTBE) assumptions for contaminated soils should be:

* C_5 -C_8 Aliphatics: 30%
* C_9 - C_{12} Aliphatics: 20%
* C_9 - C_{10} Aromatics: 50%

o For gasoline contaminated groundwater, all non-BTEX and MTBE hydrocarbons should be considered C_9 - C_{10} Aromatics.

o For "TPH" data on heavier petroleum products, the recommended default compositional parameters for contaminated soils are presented in Table 12.

Table 12 - Proposed Default Compositional Assumptions for Soil

PETROLEUM PRODUCT	DEFAULT COMPOSITIONAL ASSUMPTIONS		
	C_{10} - C_{22} AROMATICS	C_9 - C_{18} ALIPHATICS	C_{19} - C_{35} ALIPHATICS
Diesel/#2 & Crankcase Oil	60%	40%	0%
#3 - #6 Fuel Oil	70%	30%	0%
Kerosene & Jet Fuel	30%	70%	0%
Unknown Oil	100%	0%	0%

o For "TPH" data on heavier petroleum products in groundwater, all non-targeted (PAH) hydrocarbons should be considered C_{10} - C_{22} Aromatics.

o Default assumptions may not be used if actual fractional data is available, or if an LSP has reason to believe that the aromatic content may be higher than default values.

o Deviations from default values should **not** be allowed for Method 1 evaluations, but should be allowed, with justification, as part of a Method 3 assessment.

o Additional and/or modified default assumptions should be considered in the future based upon additional information and justification.

o Modified default assumptions should also be considered for screening techniques that can better define aromatic constituents.

(6) REMEDIATION WASTES

ISSUE: What role, if any, should the new VPH/EPH approach and methods have in the characterization and classification of Remediation Wastes?

DISCUSSION: Policies and permits addressing Remediation Wastes often reference a "TPH" standard. At issue is whether these references should be changed to VPH or EPH, and what the implications of such an action would be.

At present, most TPH standards addressing landfill cover and asphalt batching operations are not strictly risk-based. In terms of asphalt batching and other treatment/immobilization actions, the exposure and toxicological assumptions inherent in the VPH/EPH approach are not particularly relevant or applicable. Relative to landfill cover standards, however, VPH/EPH methods and fractional standards may be more appropriate, and could be used in a risk evaluation of fence-line receptors.

RECOMMENDATION: As part of setting risk-based standards for landfill cover, the use of the new VPH/EPH approach is recommended. For asphalt batching operations and permits, switching to a VPH/EPH standard does not seem useful or appropriate. The more germane issue in such cases is the degree of immobilization and/or treatment, an area that requires more investigation and evaluation.

It order to minimize the amount of analytical testing required, the MCP should be modified to define "TPH" as the sum of VPH and EPH hydrocarbons.

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ATTACHMENT A

REFERENCE MATERIALS AND CITATIONS
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